PAULING, L. & HUGGINS, M. L. (1934). *Z. Krystallogr.* **87**, 205.

PENNEY, W. G. & SUTHERLAND, G. B. M. (1934*a*). *Trans. Faraday Soc.* **30**, 898.

PENNEY, W. G. & SUTHERLAND, G. B. M. (1934*b*). *J. Chem. Phys.* **2**, 492.

ROBERTSON, J. M. (1943). *J. Sci. Instrum.* **20**, 175.

ROBERTSON, J. M. & WHITE, J. G. (1946). *Proc. Roy. Soc.* A, **190**, 329.

SCHOMAKER, V. & STEVENSON, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

SHAND, W. (1946). Ph.D. Thesis, California Institute of Technology.

SHANLEY, E. S. & GREENSPAN, F. P. (1947). *Industr. Eng. Chem.* **39**, 1536.

ZUMWALT, L. R. & GIGUÈRE, P. A. (1941). *J. Chem. Phys.* **9**, 458.

Acta Cryst. (1951). **4**, 20

The Structures of the Plagioclase Felspars. I

BY W. F. COLE*, H. SÖRUM† AND W. H. TAYLOR

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 29 *March* 1950)

X-ray diffraction patterns have been obtained for plagioclases of different compositions from nearly pure albite to nearly pure anorthite, and the positions of the subsidiary reflexions observed for materials with more than 30 % anorthite have been determined.

Detailed analysis of the patterns of anorthite type, obtained from materials with more than 70 % anorthite, reveals complexities not yet fully explained, while confirming the results previously obtained by Chao & Taylor.

The variation in the positions of the subsidiary reflexions given by intermediate plagioclases is discussed in detail, especially in relation to the chemical composition of the material. Preliminary experiments show that the subsidiary reflexions may be modified by heat treatment, and some consideration is given to the significance of Köhler's classification of plagioclases into high-temperature and low-temperature groups.

Possible structural schemes for the complete plagioclase series are considered, and a detailed discussion of a model for the intermediate plagioclases is to be given in Part II.

1. Introduction

The plagioclase felspars present a very complex series of structures for analysis by X-ray diffraction methods. The structure of albite ($NaAlSi_3O_8$) was determined with moderate accuracy by Taylor, Darbyshire & Strunz (1934), and shown to be essentially similar to that of orthoclase ($KAlSi_3O_8$), the differences corresponding to a slight collapse of the tetrahedron framework around the smaller cation in albite. The same authors pointed out that though anorthite ($CaAl_2Si_2O_8$), the other 'end-member' of the plagioclase series, also has a similar structure, the true periodicity in the direction of the *c* axis is 14 A., twice that of albite. Chao & Taylor (1940) showed that for some plagioclases with compositions around 60 % anorthite, 40 % albite, a characteristic feature was the appearance of pairs of weak subsidiary layer lines in oscillation photographs around the *c* axis, in place of the single subsidiary layer lines in the corresponding anorthite patterns. The general features of these patterns for intermediate plagioclases were interpreted by analogy with an optical model corresponding to an alternation, in the direction of the *c* axis, of slabs of albite-like and anorthite-like structure.

Many details of the experimental observations remained unexplained, the number of materials examined was insufficient to cover the whole range of composition of the plagioclases, and it has long been clear that there was need for a further development of the exploratory researches which terminated in 1940. In the meantime, in recent years a distinction has been established between high-temperature and low-temperature plagioclases (see, for example, Köhler, 1949), and 'subsidiary reflexions' of various kinds have been observed in the X-ray patterns of a large number of crystals. Thus, on the one hand, the scope of the problem is broadened by the necessity of considering the effects due to differences in the thermal history of the specimens, but, on the other, the successful treatment of a number of cases where a complex structure gives rise to subsidiary reflexions encourages the hope that a fairly detailed explanation may be found for the patterns given by plagioclases.

The present paper reports the results of a new examination of the plagioclases, which has enabled some progress to be made and at the same time has defined more clearly the questions still remaining unanswered.

---

* Now at Building Research Section, Commonwealth Scientific and Industrial Research Organization, Highett S. 21, Victoria, Australia.

† Now at Fysisk Institutt, Norges Tekniske Høgskole, Trondheim, Norway.

Part I is concerned chiefly with the recording and interpretation of the new experimental observations. Part II describes the development of a model which, though similar to it, supersedes that originally proposed by Chao & Taylor for the intermediate plagioclases.

2. The experimental data

We are indebted to Prof. R. C. Emmons for most of our crystalline materials, and for the information collected in Table 1. We have also received specimens (described at the appropriate points in the text) from Prof. C. E. Tilley, Dr E. Spencer, and Dr F. A. Bannister, to whom we are glad to express our thanks.

The principal aim of the experimental work has been to measure, as accurately as possible, the positions of the subsidiary layer lines in oscillation photographs (about various axes) of plagioclases of accurately determined chemical composition, covering the whole of the range from albite to anorthite.

The positions of the subsidiary layer lines are measured relative to the principal layer lines, and are expressed in terms of an angle δ_a, δ_b or δ_c, for oscillation around the a, b or c axis. The distance between principal layer lines is taken to be 360°, and for an apparent axial length N times that of albite, if the first subsidiary layer line to be occupied by reflexions is the mth of the set of $(N-1)$ lying between consecutive principal layer lines, then $\delta=(m/N)\,360°$. Thus for anorthite, with doubled c axis, $\delta_c=180°$, and for intermediate plagioclases the smaller the value of δ, the more widely separated are the two occupied subsidiary layer lines between consecutive principal layer lines. Measurements made relative to the principal layer lines on the same photograph are free from many of the usual experimental errors, and comparison of the results of repeated measurements on the same layer lines, and of independent measurements on different layer lines of the same pattern, suggests that the error in the determination of δ_a, δ_b or δ_c is not greater than $\pm 1°$, and may probably be less than this.

The determination of the chemical composition is a matter of great difficulty. Different fragments from the same sample may vary in composition by as much as 10 % in the molecular percentage of anorthite, so that chemical analysis and refractive-index measurements on the material in bulk must be supplemented by examination of the actual fragment used to obtain the diffraction pattern. The requirement that the crystal specimen must be free from twinning reduces the number of optical methods which may be applied, but in general the composition has been determined from measurements of the extinction angles on (010) and

Table 1. *Origin and chemical composition of plagioclase samples supplied by Prof. R. C. Emmons*

Sample no.	Label no.	Chemical composition expressed as weight percentage of anorthite: (*a*) From refractive index	(*b*) From chemical analysis	Origin
1	FD 1 A	77	77·1	Split Rock Point, Minn.
2	1 B	78–81	76·6	Split Rock Point, Minn.
3	10	15	11·3	Peekskill, N.Y.
4	24	41–49	48·7	Essex Co., N.Y.
5	22	66–70	70·0	Wichita Mts., Oklahoma
6	51	68–72	70·1	Duluth, Minn.
7	52	62–65	64·2	Duluth, Minn.
8	54	69–71	70·6	Duluth, Minn.
9	73	17–18	15·9	Parishville, N.Y.
10	61	70	69·8	Lake Co., Oregon
11	64	29–39	36·0	San Luis, Obispo Co., Cal.
12	87	3–6	0·2	Keystone, S.D.
13	92	51	56·1	Eland, Wis.
14	94	17–20	19·2	Tigerton, Wis.
15	97	51–53	56·3	Tigerton, Wis.
16	132 {685–695	40–48	51·4	Shelby, N.C.
17	132 {706–710	—	60·1	Shelby, N.C.
18	134	—	66·1	Chester Co., Pa.
19	144	30–34	37·7	Crestmore, Cal.
20	151	47–48	52·0	Fresno Co., Cal.
21	152	29–31	35·6	Plumas Co., Cal.
22	156	16–18	16·4	Llano Co., Texas
23	109	78	78·3	Transvaal, S. Africa
24	165	67–75	73·5	Lincoln Co., Wis.
25	166	78–80	81·3	Merrill, Wis.
26	167	53–56	59·4	Merrill, Wis.
27	53	62–77	59·7	Duluth, Minn.

In the above table, the chemical composition is quoted as weight percentage of anorthite. In deriving the composition from refractive-index measurements, the Wright felspar curves were used (see, for example, Winchell, 1933). The percentage of anorthite was deduced from the chemical analysis after allowance had been made for the presence of certain impurities, and represents an average value for the sample. For all the above data we are indebted to Prof. R. C. Emmons.

(001) for the specimen used to obtain the X-ray pattern. (The validity of this method is discussed later—see, especially, § 5 (iii).) Throughout this paper, except in Table 1, compositions are expressed as molecular percentages of the end-members albite and anorthite.

Lattice constants ($a, b, c, \alpha, \beta, \gamma$) have been measured for some plagioclases with high accuracy by the θ method and the extrapolation method (Weisz, Cochran & Cole, 1948), partly for subsequent use in the accurate structure analyses contemplated for albite and anorthite, partly in the hope that some one or other of the lattice constants would provide an unequivocal and accurate indication of the chemical composition of a plagioclase crystal under examination.

Table 2 lists the observed values of δ_a, δ_b, δ_c for the specimens examined, with the compositions (expressed as molecular percentage of anorthite) deduced from extinction angles measured for these specimens. Table 3 contains a small selection of layer-line measurements made for oscillation around axes other than the unit-cell axes a, b, c; the subsidiary reflexions appear on layer lines at the positions to be expected from the observed values of δ_a, δ_b and δ_c. The lattice-constant measurements are collected in Table 4.

Table 2. *Extinction angles, chemical composition, and positions of subsidiary layer lines in photographs about a, b and c axes*

Sample no.	Specimen no.	Extinction on (010) (°)	Extinction on (001) (°)	Molecular % anorthite	Positions of subsidiary layer lines		
					δ_a(°)	δ_b(°)	δ_c(°)
1	1	30·0	—	71·5	—	—	180
2	1	32·0	—	75·5	—	—	180
4	1	14·3	—	48	25·5	18–20	137
4	2	~10	2·9	44	24	—	140
5	1	—	—	—	—	44	160·5
5	2	29·1	—	69·5	—	—	158
5	3	27·1	—	66·5	—	—	161
7	1	29·3	—	70	—	—	161·5
8	1	—	19·1	74	—	—	180
10	1	30·0	—	71·5	—	—	180
11	1	2·1	—	31	—	—	~160
13	1	—	—	—	22·5	21·5	140
13	2	—	—	—	26·5	18	136
13	3	—	—	—	22·5	21·5	140
13	4	—	—	—	17	21·5	141·5
13	5	—	—	—	24·5	20	139
13	6	—	—	—	—	—	138·5
15	1	(22·9)	—	—	—	—	139·5
16	1	—	—	—	—	—	138
17	1	—	—	—	14	28·5	147
17	2	23·7	—	61	18	27·5	144
17	3	22·2	—	59	—	—	145·5
18	1	27·6	—	67·5	—	—	156·5
19	2	5·8	—	37·5	—	—	(See text)
21	1	~ 0·5	—	~30	—	—	0
22	1	+10·1	—	16·5	—	—	0
23	1	30·2	—	72	—	—	180
25	1	—	16·9	71	—	—	161·5
26	1	—	—	—	—	—	138·5
26	2	25·7	—	64	—	—	142

In the above table, the molecular percentage of anorthite, deduced from the measured extinction angles using the curves given by Rogers & Kerr (1942, p. 240), is quoted to the nearest 0·5 %. All extinction angles are negative except for sample 22, specimen 1, where the angle is positive, and sample 21, specimen 1, where the sign is uncertain. The values of δ_a, δ_b and δ_c are quoted to the nearest 0·5°; the error does not exceed ± 1° and is probably less than this. The extinction for sample 15, specimen 1, is apparently anomalous; the diffraction pattern for sample 19, specimen 2, is also abnormal; both cases are discussed in the text.

Table 3. *Subsidiary layer lines for oscillation around various axes*

Sample no.	Specimen no.	Rotation axis [*uvw*]	Positions of subsidiary layer lines (δ_{uvw}) (°)			
			Observed		Calculated	
			First	Second	First	Second
13	3	$10\bar{1}$	118	242	117·5	242·5
		011	161	199	161·5	198·5
		$01\bar{1}$	119	241	118·5	241·5
		102	57·5	302·5	57·5	302·5
		$10\bar{2}$	101·5	258·5	102·5	257·5
13	2	011	118	242	118	242
17	1	110	317·5	402·5	317·5	402·5
		102	50·5	309·5	52	308
		103	93·5	266·5	95	265
5	1	110	326	394	327	393

The indices [*uvw*] of the rotation axis are given with reference to the principal axes a, b, c, i.e. $c \sim 7$ A., of the cell. The calculated positions of the subsidiary layer lines are derived from the expression $u\delta_a + v\delta_b + w\delta_c = \delta_{uvw} \pm n.360$.

Table 4. *Lattice constants of plagioclase felspars*

Sample no.	Specimen no.	Molecular % anorthite	d_{100}(A.)	d_{010}(A.)	d_{001}(A.)	α^*	β^*	γ^*
Albite		~ 0	7·2791	12·7531	6·3889	86°25·1′	63°34·1′	90°27·3′
4	1	48·0	7·3258	12·8334	6·3649	86°12·5′	—	88°25·9′
13	5	~ 55	7·3299	12·8292	6·3593	86° 8·3′	63°51·8′	88°29·6′
†13	5T	~ 55	7·3220	12·8443	—	—	—	87°30·0′
13	4	~ 55	—	12·8309	—	86° 5·5′	—	88°24·5′
17	2	61	7·3318	12·8324	6·3604	85°59·2′	—	88°13·2′
5	2	69·5	7·3354	12·8378	—	—	—	88° 0·8′
1	1	71·5	—	12·8359	—	—	—	87°32·2′
Anorthite		~100	7·3492	12·8406	6·3594	85°53·3′	64° 1·8′	87° 6·2′

Sample no.	Specimen no.	Molecular % anorthite	Lattice parameters		$a:b:c$	Volume of cell (A.^{3})	Density (calc.) (g.cm.$^{-3}$)	Density (experimental) (g.cm.$^{-3}$)
Albite		~ 0	$a=$ 8·1353 $b=$ 12·7883 $c=$ 7·1542	$\alpha=$ 94°13·6′ $\beta=$ 116°31·2′ $\gamma=$ 87°42·5′	0·63615 : 1 : 0·55943	664·16	2·6241	2·6280
13	5	~ 55	$a=$ 8·1648 $b=$ 12·8585 $c=$ 7·0973	$\alpha=$ 93°33·7′ $\beta=$ 116° 5·8′ $\gamma=$ 89°47·1′	0·63497 : 1 : 0·55195	667·64	2·6850	—
Anorthite		~100	$a=$ 8·1768 $b=$ 12·8768 $c=$ 7·0845	$\alpha=$ 93°10·0′ $\beta=$ 115°50·8′ $\gamma=$ 91°13·3′	0·63500 : 1 : 0·55018	669·42	2·7592	2·760

In the above table, the molecular percentage of anorthite is determined from the extinction angle on (010) for sample 4, specimen 1; sample 17, specimen 2; sample 5, specimen 2; sample 1, specimen 1 (compare Table 2). For sample 13, specimens 4 and 5, the approximate value 55 % anorthite is derived from the figures quoted in Table 1, no extinction-angle measurements being available. The albite is from Kodarma, and is designated 'specimen T' by Spencer (1937); it contains 98 % $NaAlSi_3O_8$. The anorthite is from an olivine–biotite limestone block from Monte Somma, Vesuvius (reference number B.M. 49465; see Taylor *et al.* 1934) and is probably nearly pure $CaAl_2Si_2O_8$.

The axial lengths are calculated in Ångström units. The accuracy is ±0·0005 A., ±1′ for all except sample 1, specimen 1; sample 13, specimen 4; and sample 13, specimen 5, after heat treatment; for these three the accuracy is ±0·001 A., ±2′, the θ method alone having been used.

The values of d_{001} and c refer to the principal axes in all cases: thus, for example, for anorthite the length of the true c axis is $2 \times 7{\cdot}0845$ A.

† The heat treatment to which sample 13, specimen 5, was subjected in preparing 13, 5T is described in the text (§ 5 (iv) (*a*)).

The density of sample 13, specimen 5, may be assumed as 2·70 g.cm.$^{-3}$, from measurements made by Taylor *et al.* (1934) on similar material.

3. The albite structure

Chao & Taylor (1940) showed that plagioclases containing up to 22 % anorthite are structurally isomorphous with pure albite, but were unable to fix the limit of isomorphism. We find that samples numbered 3, 9, 12, 14, 21, 22 (Table 1), containing various proportions of anorthite up to about 30 %, are isomorphous with albite. Oscillation photographs, around the c axis, of sample 11, specimen 1, which also contains approximately 30 % anorthite (Table 2), show a few exceedingly weak subsidiary reflexions of the kind characteristic of intermediate plagioclases (see also § 5). The limit of isomorphism may thus be fixed near 30 % anorthite. The position of this limit, when very weak subsidiary layer lines first appear, cannot be determined with an accuracy comparable to that obtained for anorthite. For in the latter case, the limit when the anorthite-type changes to the intermediate-type structure is marked by the abrupt change from single subsidiary layer lines to pairs of subsidiary layer lines, and for both these structure types the subsidiary reflexions are moderately intense.

A redetermination of the atomic structure of pure albite, using the most accurate modern techniques, is urgently required as a basis for the accurate analysis of the anorthite structure, and is to be undertaken in this laboratory.

4. The anorthite structure

According to Chao & Taylor (1940) the range of isomorphism of the anorthite structure extends to a point between 80 and 67 % anorthite. Samples 1, 2, 8, 10, 23, with amounts of anorthite from 71·5 to 75·5 %, show the single subsidiary layer lines in c-axis photographs characteristic of the anorthite structure, while samples 7 and 25, with 70 and 71 % anorthite, show the pairs of subsidiary layer lines characteristic of intermediate plagioclases. The limit of isomorphism may therefore be fixed as close to 72 % anorthite (but see § 5 (iv)—thermal effects).[‡]

Table 4 confirms that there are characteristic differences in axial lengths a, b, c for albite and anorthite as reported by Taylor *et al.* (1934), and also by Chao & Taylor (1940); the new measurements are, of course, much more accurate.

[‡] Köhler (1949) states that the curves of extinction versus composition are not widely different, at high anorthite contents, for low-temperature and high-temperature plagioclases; the compositions quoted here may, therefore, be fairly reliable.

So far, the new measurements confirm, and add precision to, the earlier findings. The following observations reveal complexities not previously suspected:

(i) *The symmetry of the anorthite cell*

In c-axis photographs the principal layer lines correspond to the pseudo-axis of length ~ 7 A., the subsidiary layer lines indicate that the true axis is twice as long. Thus if we assign indices with reference to the true cell ($a \sim 8$, $b \sim 13$, $c \sim 14$ A.), for the principal layer lines in c-axis photographs l is even, for the (relatively weak) subsidiary layer lines l is odd.

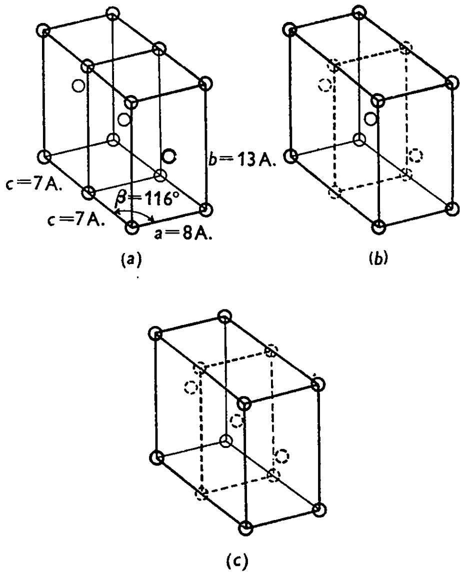

Fig. 1. Relationships of unit cells of albite and anorthite. (a) Two unit cells of albite, $c \sim 7$A., centred on (001). (b) One unit cell of 72% anorthite, $c \sim 14$A., body-centred. (c) One unit cell of pure anorthite, $c \sim 14$A., primitive. Circles and straight lines drawn in full line mark lattice points and unit-cell edges; broken lines indicate elements of pseudo-symmetry in (b) and (c).

For sample 1, specimen 1 (71·5 % anorthite), $(h+k+l)$ is even for *all* reflexions and the true unit cell is therefore body-centred. For the nearly pure anorthite specimen B.M. 49465 (see Table 4) additional reflexions occur when l is odd for which $(h+k)$ is not odd, and also a few when l is even for which $(h+k)$ is not even; for this specimen, therefore, the true unit cell is not body-centred but primitive. If these two specimens are assumed to be characteristic of the ends of the range of existence of the anorthite-type structure (from 72 to 100 % anorthite) we have a progressive reduction in symmetry from the albite cell with $c \sim 7$ A., centred on (001), to the body-centred cell with the doubled c axis for 72 % anorthite, and then to the primitive cell with doubled c axis for pure anorthite. The relationships of these cells are illustrated in Fig. 1. We do not know whether the change from the body-centred to the primitive anorthite structure takes place discontinuously or by the gradual appearance of the additional reflexions on passing from 72 to 100 % anorthite; further specimens, within this composition range, are under examination.

It must not be forgotten that the pseudo-cell (with $c \sim 7$ A.), and the pseudo-symmetry, are the same throughout, and that all these subtle differences in structure are revealed by the occurrence of subsidiary reflexions, all of which are weak, some very weak indeed.

The significance of the above observations is not yet clear, but a tentative interpretation is discussed in § 6.

(ii) *The intensities of the subsidiary reflexions*

Visual inspection of the photographs suggests that the average intensity of the subsidiary reflexions (l odd, referred to the true cell with $c \sim 14$ A.) diminishes as the proportion of anorthite decreases to 72 %. This observation, if confirmed by photometric measurement, is of interest in relation to the effects observed with plagioclases of the 'intermediate' type, discussed below (§ 5 (ii)).

(iii) *The effect of heat treatment*

Köhler's researches have shown that the optical properties of high-temperature and low-temperature plagioclases are significantly different (see also § 5 (iii)). The results described in § 5 (iv)) show that the diffraction patterns of some 'intermediate' plagioclases are modified by prolonged heating. It is obviously of interest to examine what effect, if any, is produced by heating plagioclases with anorthite-type structure.

On heating pure anorthite (B.M. 49465) for 30 hr. at 1100° C., followed by a quench, the reflexions lying on subsidiary layer lines (in c-axis patterns) are apparently unaffected (see also Raaz, 1947). We have not yet made sufficiently detailed experiments to enable us to decide whether this treatment affects those few exceedingly weak subsidiary reflexions which (in the unheated material) show that the true symmetry is not body-centred, but primitive. Specimens in the range down to 72 % anorthite have not yet been examined in this way, and it must be remembered that the specimen tested (B.M. 49465) is of volcanic origin—i.e. presumably cooled rapidly after high-temperature formation.

A plagioclase described by Hutchinson & Smith (1912) (see also Tsuboi, 1923; Smith, 1928) would be expected to behave as an 'intermediate' plagioclase, in view of its composition (5 % orthoclase, 33 % albite, 62 % anorthite). Actually it gives a pattern of anorthite type, but with abnormally weak and unusually diffuse subsidiary reflexions; it is possible that this apparently anomalous pattern is a consequence of the thermal history of the specimen. In any case, assuming that our chemical compositions are fairly accurately determined, it is clear that chemical composition alone is not sufficient to determine the structure type.

5. The intermediate plagioclases

The new data will be related both to the work of Chao & Taylor (1940) and to the experimental observations, described above, on albite and anorthite.

(i) *The subsidiary reflexions*

The characteristic feature of c-axis photographs is the occurrence of subsidiary reflexions on a pair of layer lines lying symmetrically on either side of, and rather close to, a position midway between the principal layer lines corresponding to the pseudo-axis $c \sim 7$ A. (Chao & Taylor, 1940). In Table 2 the values of δ_c, for the first member of such a pair, are quoted for some twenty specimens, and it seems clear that the separation between the two members of a pair of subsidiary layer lines varies continuously, not in a series of discrete steps. That this is so may also be seen if the subsidiary layer lines are assumed to be two of the set corresponding to a true c axis which is an integral multiple Nc of the axial length $c \sim 7$ A. corresponding to the principal layer lines; for the values of N which must be assumed are frequently very large—up to 30.

In a-axis and b-axis photographs subsidiary reflexions lie close to, and symmetrically above and below, the principal layer lines; the values of δ_a and δ_b corresponding to the subsidiary layer lines on which the reflexions lie are quoted in Table 2 for ten specimens, and again it would seem that the separation of a pair of subsidiary layer lines varies continuously.

It should be emphasized that the above conclusions depend only on the accuracy of measurement of the layer-line positions (see § 2); the accuracy claimed is confirmed by the measurements on photographs around other axes (see Table 3).

The relationships between δ_a, δ_b, δ_c are discussed in § 5 (iii) (b).

(ii) *The indices and intensities of the subsidiary reflexions*

The subsidiary reflexions frequently* occur in pairs, one on each of the pair of associated subsidiary layer lines; moreover, each such pair corresponds to a single subsidiary reflexion of the anorthite-type structure. Thus in sample 1, specimen 1 (71·5 % anorthite) the subsidiary reflexions have indices (hkl) with $(h+k)$ odd, l odd, referred to the true unit cell with $c \sim 14$ A., and the corresponding pairs of reflexions in the intermediate plagioclases have (non-integral) indices

$$\left(h-\frac{\delta_a}{360},\ k+\frac{\delta_b}{360},\ l+\frac{180-\delta_c}{180}\right)$$

and $$\left(h+\frac{\delta_a}{360},\ k-\frac{\delta_b}{360},\ l-\frac{180-\delta_c}{180}\right).$$

The nature of this correspondence can be seen on examining photographs obtained, with identical ranges of oscillation around the c axis, from sample 1, specimen 1 (71·5 % anorthite); sample 5, specimen 2 (69·5 % anorthite); sample 17, specimen 2 (61 % anorthite); sample 13, specimen 4 ($\sim$55 % anorthite, see Table 4). It is seen that the reflexions on the principal layer lines are the same in all the photographs, and that single subsidiary reflexions in the anorthite-type structure are replaced by pairs of reflexions which become more widely separated as the percentage of anorthite decreases.

Visual examination suggests that the intensities of the subsidiary reflexions are, in general, the same for different intermediate plagioclases. If confirmed, this would be interesting, especially in relation to the probable reduction in average intensity of the subsidiary reflexions for anorthite structures with the smaller proportions of anorthite (see § 4 (ii)).

It has also been observed that when the subsidiary reflexions (in c-axis patterns) lie on layer lines corresponding to a small integral value of N (see § 5 (i)), they are as sharp and well defined as the reflexions on principal layer lines; whereas, when the value of N must be taken to be large, to correspond accurately with the observed layer-line separations, the subsidiary reflexions are markedly less well defined.

(iii) *The variation of δ_a, δ_b, δ_c with chemical composition*

Formidable difficulties are encountered in attempting to correlate the measured values of δ_a, δ_b and δ_c with chemical composition.

In the first place, as explained in § 2, it is necessary to find the chemical composition of the small untwinned crystal fragment used to obtain the diffraction pattern; this is done by measuring extinction angles on (010) and/or (001) and using standard curves of extinction angle versus composition. Köhler (1949), however, has shown that for plagioclases from volcanic rocks a different set of curves should be used in deriving composition from optical constants, and that the use of the older curves (appropriate for low-temperature plagioclases) may give anorthite contents too high by 10–15%. Köhler states that it is usually possible, with complete optical measurements, to decide whether low-temperature or high-temperature curves are appropriate, but has not yet published a comprehensive set of curves for use with high-temperature materials. In the present research it has been necessary to work from existing curves, and with untwinned material so that the chemical compositions derived from their use must be accepted with some reserve. In a footnote to the first paragraph in § 4, reasons have been given for anticipating that the old curves will give satisfactory values for plagioclases with high anorthite content.

Secondly, it seems reasonable to expect that the structural condition of the plagioclase will depend upon its thermal history as well as upon its composition, and in this case it is wrong in principle to seek a direct correlation between the δ values and composition alone. We shall see, however (§ 5 (iv) (a)), that our observa-

---

* Occasionally one reflexion of the pair is relatively much weaker than the other, or may be absent.

tions suggest that well-defined subsidiary layer lines are likely to occur in plagioclase structures of the 'intermediate' type only when the material is in or near the low-temperature state; thus, it may be found that there is in fact a direct correlation between the δ values and the composition.

(*a*) In Fig. 2 the measured values of δ_c are plotted against molecular percentage of anorthite, the method used for determining the composition being indicated in the diagram. The range of compositions between 50 and 72 % anorthite is adequately covered, but the values of δ_c do not lie closely on any simple curve; the straight line drawn in this region of the diagram should be regarded as representing only approximately the variation of δ_c with composition. A line (broken in the diagram) drawn symmetrically about the composition 50 % anorthite passes close to the three points representing observations on materials with less than 50 % anorthite. Until more is known about the interdependence of composition and thermal history, it would be unwise to attach too much significance to these symmetrical linear variations.

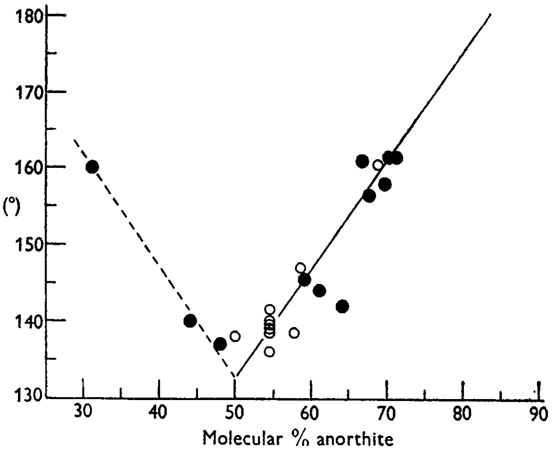

Fig. 2. Variation of δ_c with chemical composition. The values of δ_c are given in Table 2. The chemical composition is given in Table 2 for those specimens for which extinction angles were measured (denoted by black circles). For other specimens (denoted by open circles) the composition (in molecular percentage of anorthite) is deduced from the weight percentage of anorthite quoted in Table 1, column (*b*), 'from chemical analysis'.

(*b*) Fewer measurements of δ_a and δ_b are available; they may be treated in two ways. *First*, we may assume that the chemical compositions of the crystal fragments may be deduced from the measured values of δ_c by means of the straight lines of Fig. 2. Then on plotting δ_a and δ_b against composition (Fig. 3), symmetrical pairs of straight lines may again be taken to represent the variations above and below 50 % anorthite. *Alternatively*, δ_a and δ_b may be plotted directly against δ_c, for the same crystal fragments (without reference to the chemical composition), as in Fig. 4. The variation is, to a first approximation, linear for both δ_a and δ_b; δ_a decreases, and δ_b increases, as δ_c increases.

Since the points in Fig. 4 represent only measurements of the positions of the subsidiary layer lines in different photographs, this method of presentation avoids the difficulties encountered when chemical composition is considered, but it is necessarily less significant when a structural interpretation is sought in terms of the end-members albite and anorthite. Thus it does not differentiate between two plagioclases, one with more than 50 % anorthite, the other with less than 50 %, which give identical δ_a, δ_b and δ_c values. It also implies that a given value of δ_c (or δ_a, or δ_b) corresponds uniquely to a given structure, and so ignores the possibility that two specimens differing in both composition and thermal history may have identical values of δ_a, δ_b and δ_c. In the treatment represented in Fig. 3, on the other hand, it is implicitly assumed that if the measurements were made with sufficient accuracy then δ_a, δ_b and δ_c would be found to vary linearly with composition, the thermal history having no influence on any of these quantities.

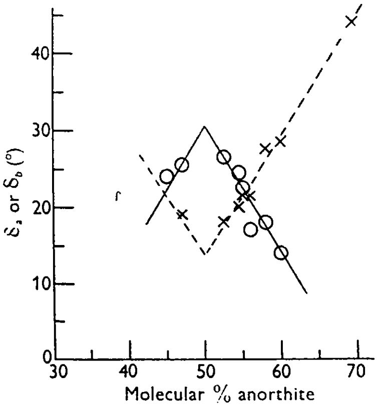

Fig. 3. Variation of δ_a (circles and full line) and δ_b (crosses and broken line) with chemical composition. The values of δ_a and δ_b are given in Table 2, the chemical compositions are deduced from the observed δ_c's by means of the straight lines of Fig. 2 (see text, § 5 (iii) (*b*)).

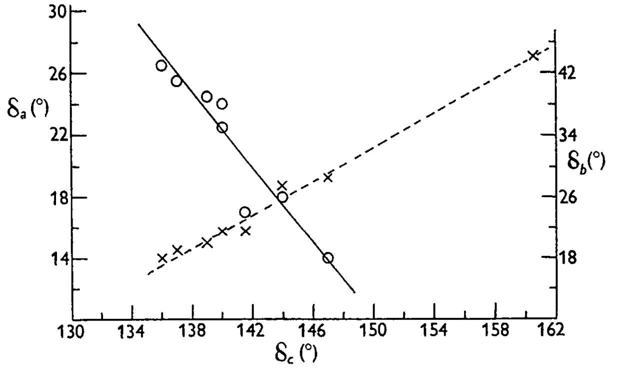

Fig. 4. Variation of δ_a (circles and full line) and δ_b (crosses and broken line) with δ_c. Note the different scales for δ_a (on left) and δ_b (on right). The values of δ_a, δ_b and δ_c are given in Table 2.

It will be clear that the data so far available are insufficient to justify either of these ways of treating the data. It is, however, convenient to have both representations for the discussion of the structural significance of our observations.

(iv) *The effect of heat treatment*

The following preliminary observations suggest that a thorough examination of the effects produced by different heat treatments would be of interest both for an understanding of the optical properties characteristic of low-temperature and high-temperature plagioclases, and in seeking a detailed explanation of the structures of the intermediate plagioclases:

(*a*) We have seen (§ 4 (iii)) that no apparent change is produced in the diffraction pattern of pure anorthite by heating for 30 hr. at 1100° C., followed by a quench. By contrast, in the case of labradorite (sample 13, specimens 4 and 5) heating for 25 hr. at 1000° C., followed by a quench, results in a considerable reduction in the intensities of subsidiary reflexions (in *c*-axis photographs), and further heating (70 hr. at 1100° C.) removes all but a few of the most intense of the subsidiary reflexions. No noticeable recovery in the intensities of these reflexions occurs after annealing for 150 hr. at 800° C. No obvious change in δ_c occurs as the subsidiary reflexions gradually become weaker, but this is a point which calls for fuller investigation.

A labradorite occurring as phenocrysts in a lava flow at Clear Lake, Utah, probably containing approximately 55 % anorthite, shows no subsidiary reflexions, though the composition would lead one to place the plagioclase in the 'intermediate' group.* It is reasonable to suppose that the rapid cooling from a high temperature of formation, characteristic of volcanic rocks, prevents the diffusion of calcium and sodium atoms, and so accounts for this 'anomalous' behaviour.

These experiments suggest that high-temperature plagioclases, whether natural or produced by laboratory heat treatment of low-temperature materials, do not show subsidiary reflexions. Pending further experiments, now in hand, this conclusion should be regarded as provisional. The need for caution is emphasized by the observation (§ 4 (iii)) that a plagioclase with 62 % anorthite (and therefore well within the 'intermediate' range) gives a pattern of subsidiary layer lines of anorthite type, though the subsidiary reflexions are abnormally weak and diffuse.

(*b*) The optical properties are in harmony with the above preliminary observations on the X-ray diffraction patterns. Thus for sample 13, specimen 5, the heat treatment which (almost) removes the subsidiary X-ray reflexions results in a change in extinction angle on (010) from about 19 to 28·5°, the extinction on (001) being practically unchanged, while the labradorite from Clear Lake, Utah (which shows no subsidiary reflexions), has extinction angles 25° on (010) and 8·5° on (001). These 'anomalies' in extinction on (010) are in the direction expected for high-temperature plagioclases, according to the work of Köhler (1949). The extinction on (010) is also probably 'anomalous' for sample 15, specimen 1, which shows subsidiary X-ray reflexions ($\delta_c = 139{\cdot}5°$, see Table 2). The interpretation is not clear, though two possibilities should be kept in mind—the likelihood that plagioclases exist in states intermediate between truly low-temperature and truly high-temperature conditions, and the fact that a plagioclase with less than 50 % anorthite may have properties similar to those of a material with more than 50 % anorthite.

(*c*) The data included in Table 4 show that significant changes in d_{100}, d_{010} and γ^* are produced by the heat treatment of sample 13, specimen 5. Similar high-accuracy measurements are required for other materials, for correlation with the optical data and the observations on the subsidiary reflexions.

(v) *Other observations*

In this section we collect a few isolated observations, the importance of which is not yet clear.

(*a*) With exceptionally long exposures, in *c*-axis oscillation photographs, additional subsidiary reflexions are observed in pairs close to, and symmetrical about, principal reflexions. Their intensity is estimated as about one-hundredth that of the 'ordinary' subsidiary reflexions, and their presence may probably be ignored in attempts to develop a simple model capable of accounting for the occurrence of reflexions characterized by δ_a, δ_b and δ_c.

(*b*) Sample 19, specimen 2, shows pairs of relatively intense extra reflexions, in *c*-axis photographs, off the principal layer lines, but not in positions corresponding to pairs of subsidiary layer lines as in other intermediate plagioclases. No certain explanation has been found for their occurrence, though twinning in the crystal fragment is clearly a possibility.

(*c*) The measurements of lattice dimensions collected in Table 4 are too incomplete to warrant detailed discussion, but attention may be directed to certain interesting features.

First, the lengths of the principal axes of sample 13, specimen 5, are nearly identical with those of anorthite and differ appreciably from those of albite. This is in agreement with the findings of Chao & Taylor (1940) which were based on measurements of lower accuracy. It would be interesting to know whether the axial lengths *a*, *b*, *c* change gradually or suddenly, and how the change is related to the pattern of subsidiary reflexions.

Secondly, the effect of heat treatment on sample 13, specimen 5, is to cause appreciable changes in d_{100}, d_{010} and γ^*—the only quantities measured for the heat-treated material.

6. Interpretation of the experimental data

The experimental data recorded in the preceding sections, though incomplete, serve to demonstrate the

---

* We are indebted to Dr E. Spencer for this material, and for suggesting that it might give an abnormal X-ray pattern.

complexity of this series of structures and to confirm the importance of the thermal history of a plagioclase in determining its constitution. They also permit the consideration of a tentative structural interpretation, and can be correlated with some of the generalizations made in Köhler's recent discussion of the optical evidence adduced in support of his division of plagioclases into low-temperature and high-temperature types.

(i) *Albite*

Our study of the plagioclases emphasizes the need for a high-accuracy redetermination of the atomic structure of albite. In view of the statement of Köhler (1949) that 'at the albite end [of the plagioclase series] the differences are slight' (between high-temperature and low-temperature curves of optical constants versus composition), a fuller account of the work of Tuttle & Bowen (1949) is awaited with much interest. A brief summary of their results reports that synthetic albite has optical and X-ray properties notably different from natural albite of granite and pegmatites, but like those of albite from some volcanic rocks, and that on prolonged heating at high temperatures pegmatitic albite inverts to a modification identical with the synthetic material. These observations may also be of great interest in relation to the problem of the precise constitution of the soda-felspar lamellae in perthitic potash–soda felspars.

(ii) *Anorthite*

When an accurate analysis of the albite structure has been completed, it will be possible to determine the structure of an anorthite with similar accuracy. In addition, however, it is necessary to find an explanation for the small but significant difference between the body-centred cell at 72 % anorthite and the primitive cell at 100 % anorthite, and for the abrupt change (at 72 % anorthite) from the anorthite-type to the intermediate-type structure. Our experimental observations are not at present sufficiently complete and detailed to enable us to provide a unique explanation, but at least two alternative models may be considered.

First, if the variation in δ_c observed up to 72 % anorthite were continued to $\delta_c = 180°$ (i.e. where the pair of subsidiary layer lines of the intermediate type would merge and become a single subsidiary layer line), then on any reasonable assumption about the variation of δ_c with composition this limit would be reached between 80 and 90 % anorthite, say at 85 % anorthite (the straight line of Fig. 2 would give 83 %). The region 100 to 85 % anorthite is then one of true isomorphous substitution, in which random replacement of calcium and aluminium by sodium and silicon atoms raises the true symmetry from primitive to body-centred. The region 85 to 72 % anorthite is, however, a disordered structure of two 'phases', one the body-centred anorthite type, the other the albite type; the small number of unit cells of albite type are stacked at random among the anorthite-type cells, and so the diffraction pattern remains characteristic of the latter. At 72 % anorthite the number of albite-type cells is, for the first time, sufficient to bring about an ordered interstacking of the two types, and the pattern characteristic of intermediate plagioclases appears.

Alternatively, it is possible to develop a model in which the whole range 100 to 72 % anorthite corresponds to isomorphous substitution, with the associated symmetry change. Below 72 % the high-temperature material corresponds either to a disordered structure of the two phases (with anorthite-type pattern) or to the 'freezing-in' of the albite-type structure (with face-centred cell, no subsidiary reflexions, and c axis ~ 7 A.); the low-temperature material in this composition range is an ordered structure of the two phases, giving the intermediate-type diffraction pattern. In this case, the 'discontinuity' at 72 % anorthite represents nothing more than the sudden onset of the ordering process when segregation of sodium and calcium atoms leads to the formation of a regular pattern of alternating slabs of anorthite-type and albite-type structures.

Further work is now in hand to enable us to decide whether either of these models is satisfactory.

(iii) *The intermediate plagioclases*

Part II of this paper will be devoted to the development of a model consisting of alternating slabs of albite-type and anorthite-type structures. It is convenient to deal here with two aspects of this model.

First, our experiments suggest that the structural scheme of the plagioclases may be symmetrical about the mid-point of the series at 50 % anorthite. For example, the observed values of δ_a, δ_b and δ_c may be considered as varying with composition symmetrically about this point (Figs. 2, 3); again, the boundary between the albite-type structure and the intermediate-type structure is fixed near 30 % anorthite (§3), while that between intermediate and anorthite types is fixed near 72 % anorthite (§4). It is thus not unreasonable to suppose that isomorphous replacement, and/or a range of disorder of two 'phases' (albite type, anorthite type), may occur at the albite end of the series corresponding to those at the anorthite end. Further, on the assumption of symmetry about 50 % anorthite, the component slabs of albite type and anorthite type in the intermediate structure are not pure $NaAlSi_3O_8$ and pure $CaAl_2Si_2O_8$, but have compositions $(100-x)$ % albite, x % anorthite *and* x % albite, $(100-x)$ % anorthite, respectively, where (see §6 (ii)) x may be $\sim$ 15–30 but is unlikely to lie far outside these limits.

Secondly, our experiments on heat treatment support the fundamental idea that the intermediate structures are ordered superlattices; for high-temperature treatment of such a plagioclase may result in the disappearance of the characteristic subsidiary reflexions of the

X-ray pattern, as would be expected if the process is one of disordering. Köhler's measurements have, similarly, shown that on heating the low-temperature plagioclases of plutonic and metamorphic rocks their optical properties change to those characteristic of materials of volcanic origin, or prepared synthetically—i.e. cooled rapidly so as to preserve the disordered state characteristic of their high temperature of formation.

A fuller discussion of these points awaits the results of further work now in progress.

We are indebted to Prof. Sir Lawrence Bragg for his interest in this research, and to Prof. R. C. Emmons, Prof. C. E. Tilley, Dr E. Spencer and Dr F. A. Bannister for samples of plagioclases and information on their compositions and optical properties. One of us (H.S.) is indebted to the Norges Tekniske Høgskoles Fond for a grant, and to the British Council for a Scholarship, during the tenure of which this work was done.

References

CHAO, S. H. & TAYLOR, W. H. (1940). *Proc. Roy. Soc.* A, **176**, 76.

HUTCHINSON, A. & SMITH, W. C. (1912). *Miner. Mag.* **16**, 267.

KÖHLER, A. (1949). *J. Geol.* **57**, 592.

RAAZ, F. (1947). *Anz. Akad. Wiss. Wien.* **84**, 45.

ROGERS, A. F. & KERR, P. F. (1942). *Optical Mineralogy*. New York: McGraw-Hill.

SMITH, W. C. (1928). *Miner. Mag.* **21**, 543.

SPENCER, E. (1937). *Miner. Mag.* **24**, 453.

TAYLOR, W. H., DARBYSHIRE, J. A. & STRUNZ, H. (1934). *Z. Krystallogr.* **87**, 464.

TSUBOI, S. (1923). *Miner. Mag.* **20**, 101.

TUTTLE, O. F. & BOWEN, N. L. (1949). Abstracts of papers presented at 30th Annual Meeting of Mineralogical Society of America, 10–12 November 1949, p. 19.

WEISZ, O., COCHRAN, W. & COLE, W. F. (1948). *Acta Cryst.* **1**, 83.

WINCHELL, A. N. (1933). *Elements of Optical Mineralogy*. Part II. *Description of Minerals*, 3rd ed. New York: Wiley.

Acta Cryst. (1951). **4**, 29

Ein modifizierter Lorentzfaktor für Drehkristallverfahren

VON HANS GUNTHER HEIDE

Institut für Medizin und Biologie (Abt. Biophysik) der Deutschen Akademie der Wissenschaften zu Berlin, Berlin-Buch, Deutschland

(*Eingegangen am* 16. *Februar* 1950)

The usual expressions for the Lorentz factor of rotation diagrams become infinite for certain angles. This ceases to be the case if a finite region of reflecting power is taken account of in reciprocal space, corresponding to small finite coherent blocks in the crystal. Curves are calculated showing how the reflected intensity depends on the size of these blocks and on the angle of reflexion in the neighbourhood of those angles for which the usual expression is infinite.

Problemstellung

Die gebräuchlichen Ausdrücke für den Lorentzfaktor bei Drehkristallverfahren werden bekanntlich für alle die Streurichtungen unendlich, welche in der durch Primärstrahl und Drehachse gebildeten Ebene liegen. So wächst insbesondere der Faktor $L_3 = 1/(\cos\sigma \sin\tau)$ für $\tau = 0°$ oder 180° (und für $\sigma = 90°$) über alle Grenzen (σ = Schichtlinienwinkel, τ = Azimut des Reflexes). Nun können aber, bei geeignetem Verhältnis von Gitterkonstanten und Wellenlänge, sehr wohl exakt in diesen Raumrichtungen Interferenzmaxima auftreten (deren Intensitäten im Experiment tatsächlich sehr gross werden). Da der Lorentzfaktor multiplikativ in die Intensitätsformel eingeht, ist es klar, dass diese Formeln für ihn an den Punkten, an denen sie Pole besitzen, nicht mehr gültig sein können, was seine Ursache in vereinfachenden Annahmen bei deren Herleitungen hat. Es erhebt sich nun die Frage: welchen Wert hat der Lorentzfaktor an und dicht neben diesen Punkten wirklich, und wie weit kann der übliche Ausdruck als Näherung gebraucht werden? Die Beantwortung dieser Frage wird praktisch wichtig z. B. bei der Auswertung von Röntgendiagrammen hochmolekularer organischer Kristalle, wo wegen der grossen Translationsperioden praktisch immer einige Reflexe dicht bei solchen Unendlichkeitsstellen des Lorentzfaktors liegen, oder z. B. bei einer experimentellen Nachprüfung des theoretischen Lorentzfaktors durch Aufnahme ein und desselben Interferenzmaximums (*hkl*) in verschiedenen Schichtlinien oder bei verschiedenem Winkel zwischen Drehachse und Primärstrahl.

Die oben gestellte Frage ist vor längerer Zeit von Ott (1934) behandelt worden, unter Berücksichtigung der Primärstrahldivergenz bei Voraussetzung einer un-